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THERMAL PROPERTIES OF AUSTRALIAN OIL SHALES: CHARACTERIZATION BY THERMAL ANALYSIS AND INFRARED SPECTROPHOTOMETRY

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INTRODUCTION

Thermal methods of analysis such as thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are obvious choices for studying the thermal behavior and retorting properties of oil shales.

This paper describes work in which we combined TG, DTG and DSC techniques with infrared (ir) transmission spectrometry to provide pyrolysis and oxidative profiles as a means of characterizing and comparing Australian oil shales.

EXPERIMENTAL

Specimens of oil shale were obtained from the Condor, Duaringa, Julia Creek, Nagoorin, Rundle and Stuart deposits in Queensland; and from the Glen Davis and Hartley Vale torbanite deposits in New South Wales. Each specimen was ground in a Sieb mill and sieved. A sieved fraction (-1.4 to +0.6 mm) was chosen for analysis and ballmilled.

Kerogen concentrates were prepared by demineralizing the powdered oil shales with HCl and then HF solutions. Concentrates derived from Queensland shales contained 5-15% residual mineral matter with pyrite as a principal component. The torbanites do not contain pyrite and yield kerogen concentrates with less than 2% mineral matter.

TG and DTG curves were obtained by means of Cahn RH and RG thermobalances interfaced to an LSI-11 computer. Data were processed using a recursive digital filter as described elsewhere (1).

Differential scanning calorimetry was carried out using a Perkin-Elmer DTA 1700 in the DSC mode.

Solid-state ir spectra of oil shales, kerogen concentrates and residues were obtained using a pressed KBr disc technique. All spectra were measured on a JASCO A-302 ir spectrophotometer.

RESULTS AND DISCUSSION

The ir spectra of all kerogens are broadly similar. Table I lists the principal absorption bands which are common to samples of the oil shales and kerogen concentrates that we examined.

TABLE I

INFRARED SPECTRA OF KEROGENS

Band Frequency cm^{-1}	Assignment
3400	O-H stretch
2930	asym. stretch, CH_2 alkyl
2860	sym. stretch, CH_2 alkyl
1700	C=O stretch, ester, aldehyde, -COOH
1620	C-C vibration of aromatic rings
1465	asym. band of alkyl CH_3 and CH_2 groups
1375	mainly sym. band of CH_3 groups

Note: A moderately intense band at 720 cm^{-1} due to CH_2 rocking vibrations of noncyclic hydrocarbons having more than four contiguous CH_2 groups is also prominent in spectra of NSW torbanite and Duaringa kerogen.

As Rouxhet et al. have shown (2), ir spectra of coals, kerogens, humic substances and other carbonaceous solids are qualitatively alike, in the sense that they display the same major absorption bands. Nevertheless, the various kerogens display considerable differences in band intensities which permit useful qualitative comparisons. This is illustrated in Figure 1 with ir spectra of Hartley Vale and Julia Creek kerogens. The aliphatic content of Hartley Vale kerogen is high, as shown by the intensity of bands at 2930, 2860, 1455 and 1375 cm^{-1} Julia Creek kerogen, by contrast, is more aromatic, having weaker alkane bands and a correspondingly more intense aromatic band at 1620 cm^{-1}. The concentration of carboxylic groups in Julia Creek material is also much higher, as indicated by strong O-H stretching and C=O stretching bands at 3400 cm^{-1} and 1700 cm^{-1}, respectively. A comparison of ir spectra of all the kerogen specimens shows the most aliphatic material to be the kerogen components of Hartley Vale, Glen Davis and Duaringa shales. Kerogens of the Nagoorin carbonaceous and Condor carbonaceous shale are the most aromatic with ir spectra similar to those of coals. The aromaticity of Condor brown, Julia Creek and Stuart shale lies in between the extremes represented by the torbanites and carbonaceous shales.

Compositional differences revealed by ir spectrophotometry are reflected in the thermal behavior of the various kerogens, as the following discussion shows.

A common feature of kerogen pyrolysis is that decomposition of carboxylic groups dominates the early stages, from about 150 to 300°C for linear heating in nitrogen; this is indicated by a substantial reduction in O-H and C=O vibrational stretching bands at 3400 and 1700 cm^{-1}, respectively. Thus, the low concentration of -COOH groups observed for torbanite kerogen would account for the low rates of mass loss observed for Hartley Vale and Glen Davis oil shales below 300°C, as shown in Figure 2; conversely, TG-DTG pyrolysis curves for Julia Creek kerogen demonstrate that significant mass losses occur below 300°C, as one might predict from the comparatively high content of carboxylic groups indicated by the ir data of Figure 1.

Figure 3 gives TG-DTG oxidative and pyrolysis profiles for two substantially aromatic shales (Nagoorin carbonaceous oil shale and a specimen obtained from the carbonaceous sequence of the Condor deposit). TG-DTG curves are also given for two shales with a high aliphatic component: Hartley Vale shale and a specimen from the Condor brown shale unit. A notable feature is that the total mass loss for combustion of Hartley Vale and Condor brown shale is only slightly greater than that obtained by pyrolytic decomposition in nitrogen. On the other hand, the mass loss by combustion of the Nagoorin and Condor carbonaceous shale is much greater than the corresponding mass loss by pyrolysis; that is, pyrolysis of the more aromatic kerogen yields a substantial amount of combustible residue. Mass losses for both pyrolysis and oxidation are given in Table II for a number of Australian oil shales.

TABLE II

THERMOGRAVIMETRIC ANALYSIS OF SOME AUSTRALIAN OIL SHALES

Shale	Mass Loss % in air	Mass Loss % in N_2	Mass Loss Ratio Air:N_2
Hartley Vale	53.8	52.5	1.03
Rundle	28.5	26.0	1.09
Condor brown	18.7	18.4	1.02
Julia Creek	32.4	23.5	1.38
Condor carbonaceous	43.9	26.9	1.63
Nagoorin	62.5	31.8	1.97

Other compositionally dependent features are demonstrated by TG-DTG oxidative profiles. In a separate study (3) we have used TG-DTG techniques, ir transmission spectra and evolved gas analysis (EGA) to examine the oxidative properties of Australian oil shales and kerogen concentrates, and to identify the major oxidative stages in cynamic air atmospheres. This work showed that combustion of the kerogen component of shale occurs in two stages. Stage 1 involves near-complete combustion of aliphatic components, to yield a char containing aromatic moieties and (presumably) elemental carbon; and stage 2 is, therefore, combustion of the char residue. The various oxidation stages are illustrated in Figure 4 with TG-DTG curves for Condor carbonaceous, Rundle, Stuart and Julia Creek shales. Julia Creek shale shows a substantial weight loss between 650 and 800°C due to thermal decomposition of calcite and, in this respect, differs from the other shales. Common features shown in Figure 4 are two major DTG peaks at 280 and 420°C, respectively, denoting the two stages of kerogen combustion. Minor peaks at 450 (stage 3) and 600-666°C (stage 4) arise from combustion of pyrite as indicated by the following:

i. EGO measurements to 500°C (3) showed that SO_2 is the major gaseous species evolved during stage 3.

ii. Addition of pyrite to a kerogen concentrate derived from Condor brown shale enhances stages 3 and 4, as shown in Figure 5; the additional mass loss due to added pyrite is as one might expect, assuming that SO_2 and Fe_2O_3 were the products of pyrite combustion.

Although there appears a rough parallelism of ir spectra as indicators of aromaticity, as well as the ratio of the magnitudes of the first and second stages of combustion, we cannot assume that this ratio provides a quantitative measure of the ratio of aliphatic to aromatic constituents in raw shales, since heating may induce aromatization of cyclic hydrocarbons, and combustion of aromatic constituents could also occur during stage 1. But certainly, the results are consistent with a model for kerogen visualizing alkane, alkanone, carboxylic and various other reactive functional groups held within a polymeric and thermally more stable polynuclear aromatic framework.

Although we can relate TG-DTG curves to broad compositonal features of Australian oil shales, there is no immediately apparent connection between thermal properties and type of precursor material as suggested by Earnest (4, 5). For example, petrology of Rundle, Stuart and Condor brown shales (6), shows the kerogen to be primarily of algal origin, with the colonial green alga Pediastrum as a major precursor. Julia Creek oil shale (7, 8) is a marine shale with planktonic or benthonic algae, dinoflagellate and arcitarch cysts as principal originating materials. Condor carbonaceous shale (6) is derived from higher plants in a forest swamp environment. Although a substantial calcite decomposition DTG peak reflects the marine origin of Julia Creek material, all these shales show qualitatively similar thermal behavior, with quantitative differences reflecting the degree of catagenesis rather than the nature of precursor organisms.

DSC curves show that for all shale specimens that we have examined by this technique, pyrolytic decomposition of the kerogen component is a weakly endothermic event. This can be seen from the data of Figure 6 and Table III. Figure 6 shows a DSC curve for a Julia Creek oil shale sample, with an endotherm for calcite decomposition at 810°C overshadowing the pyrolysis endotherm between 390 and 610°C, although mass loss due to pyrolysis is substantial (25% compared to 18% for the calcite decomposition). Table III lists enthalpy of pyrolysis for a number of samples. For calculating the values given in column 3 as MJ/kg contained kerogen, the kerogen content was taken as the total mass loss incurred during first and second stage combustion.

TABLE III

ENTHALPY OF PYROLYSIS

Sample	Enthalpy of Pyrolysis	
	MJ/kg raw shale	MJ/kg contained kerogen
Rundle oil shale	0.22	0.91
Condor carbonaceous shale	0.13	0.37
Condor brown shale	0.21	1.20
Julia Creek shale	0.13	0.48
Hartley Vale shale	0.12	0.22
Hartley Vale kerogen concentrate	-	0.22

Although the results of Table III are preliminary and incomplete, they indicate a substantial variability in thermal behavior of the various kerogen components of Australian oil shales. These DSC measurements are continuing as a means of relating oil shale composition and thermochemical behavior.

Table II shows that pyrolysis of the more aromatic and catagenically more mature oil shales yields a carbonaceous residue that could represent a useful secondary heat source in the retorting process. With this in mind, we investigated combustion of a Nagoorin carbonaceous shale specimen and some pyrolyzed residues which were derived by linearly heating the raw shale in nitrogen to various stages of pyrolysis. Enthalpy values obtained from this study are listed in Table IV.

In a parallel study, we monitored changes in the ir spectrum of the shale at various stages of pyrolytic decomposition in nitrogen. The ir spectrum of the raw shale shows some bands due to mineral components (mainly kaolinite), but the principal bands of the kerogen component (Table I) are prominent. This kerogen is more advanced in catagenesis than the Julia Creek and Hartley Vale kerogens of Figure 1; a lower carbonyl/carboxyl functionality is evident by the 1700 cm^{-1} band appearing at reduced intensity as a shoulder to the prominent 1600 cm^{-1} band and alkyl groups are fewer as shown by comparitively weak C-H stretching bands near 2900 and 1400 cm^{-1}. Up to 580°C and 75% pyrolysis, the principal spectral changes are a diminution in the C=O band at 1700 cm^{-1} accompanied by loss of alkyl bands. At 75% pyrolysis, these bands are no longer evident. However, a band at 1620 cm^{-1} attributable to aromatic C-C vibrations, is still prominent at this stage of pyrolysis. On further pyrolysis, the aromatic band progressively diminishes and is

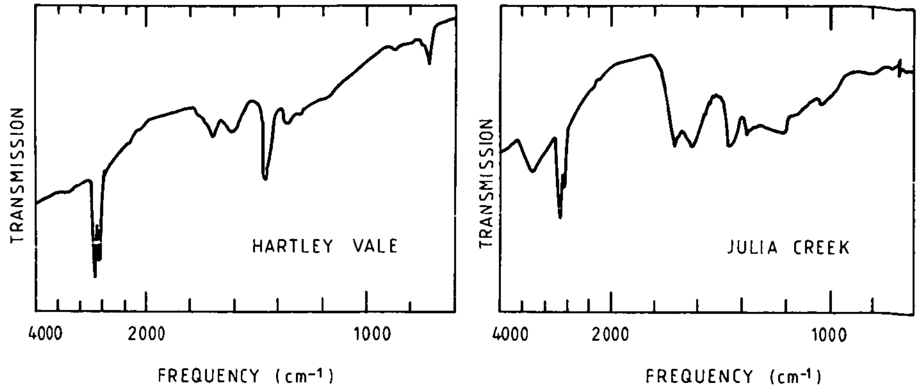

Figure 1. Infrared spectra of kerogen concentrates.

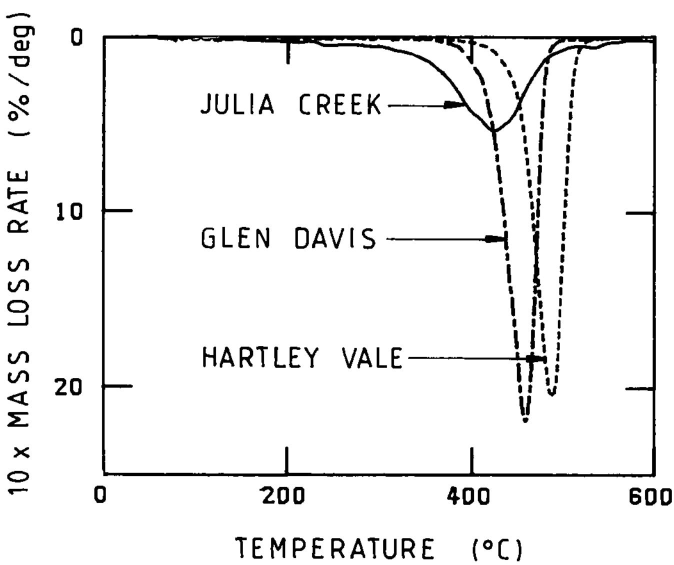

Figure 2. DTG curves for kerogens heated in nitrogen at 10°/min.

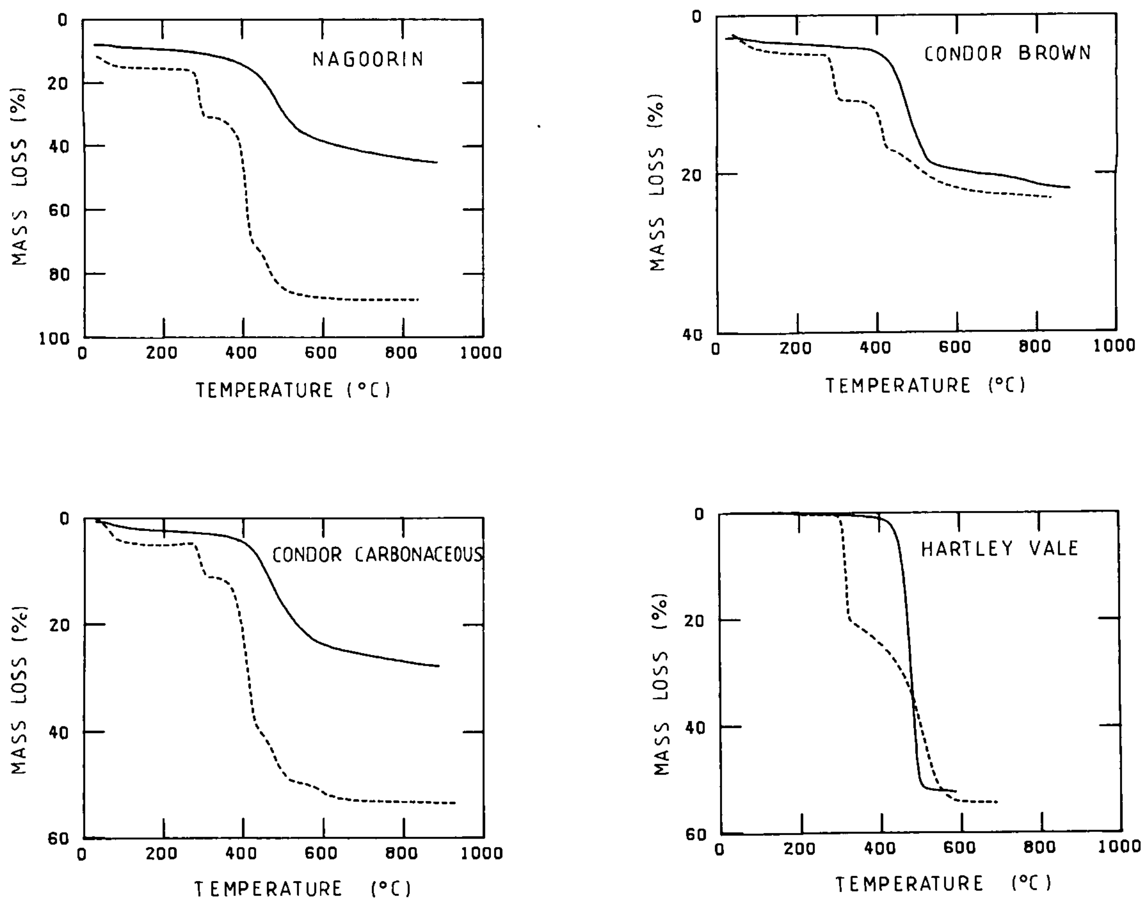

Figure 3. TG curves for Australian oil shales heated at 10°/min full curve - nitrogen, dashed curve - air.

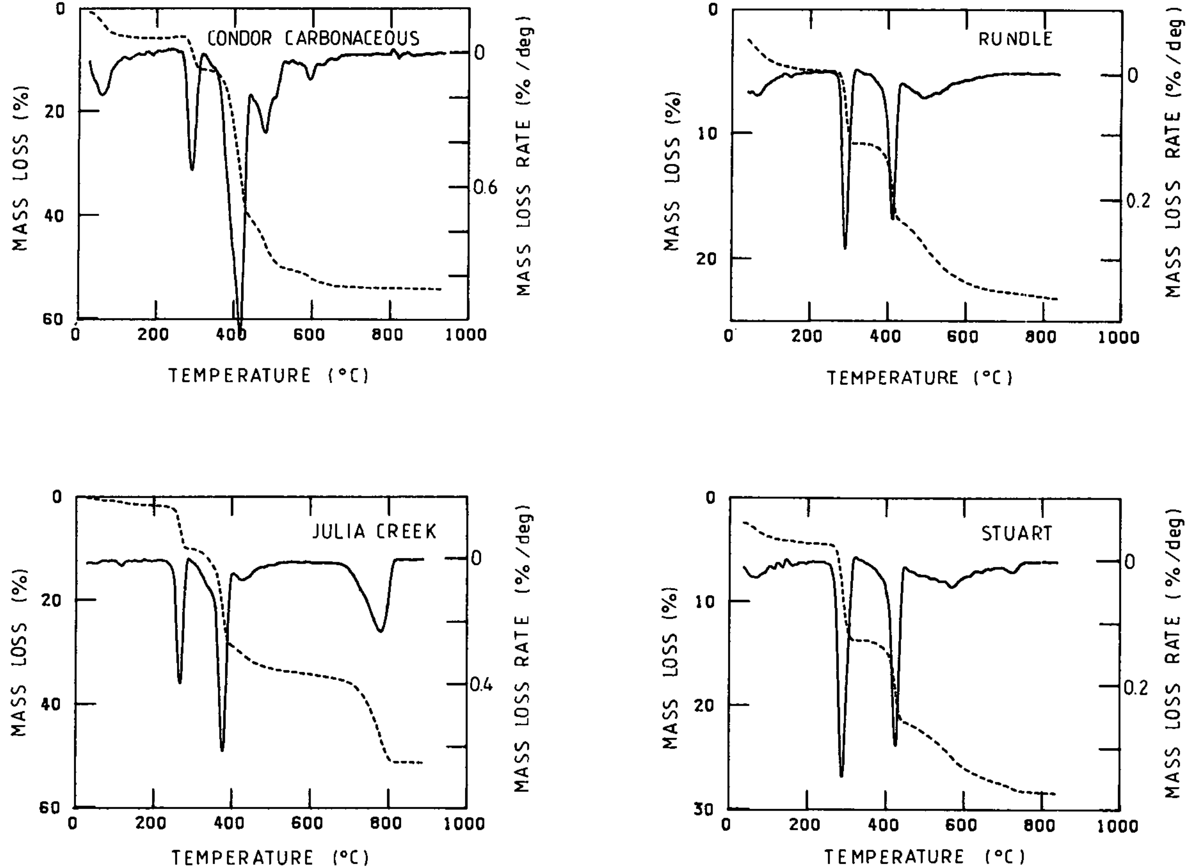

Figure 4. TG–DTG oxidative profiles for Australian oil shales heated in air at 10°/min.

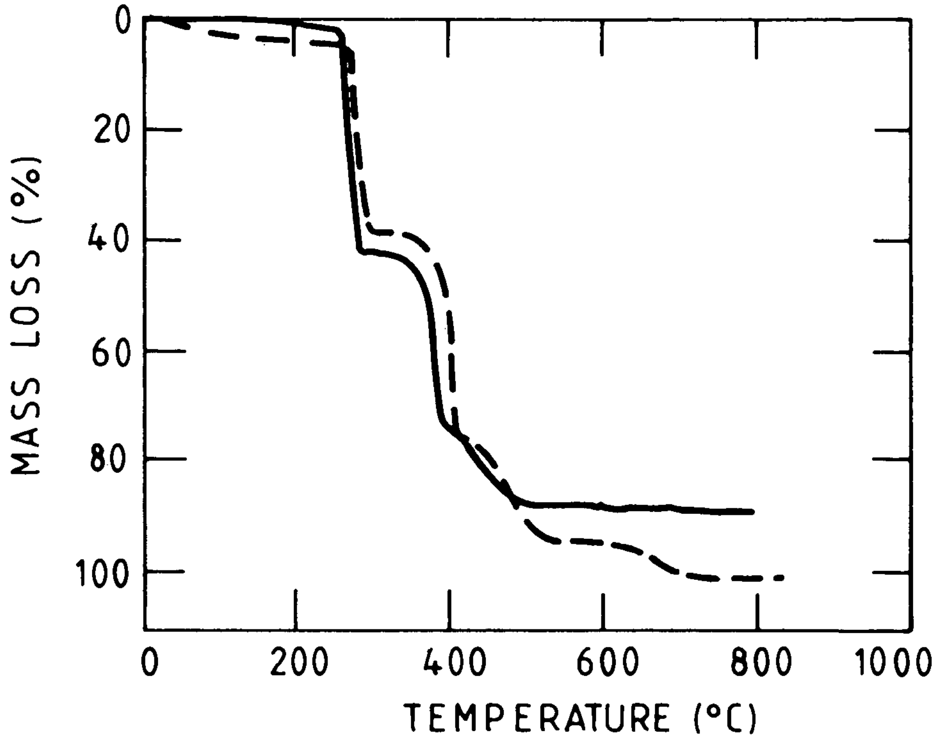

Figure 5. TG curve for Condor kerogen concentrate heated in air at 10°/min.
Full line - kerogen with no added pyrite.
Dashed line - with pyrite mixed into kerogen sample.

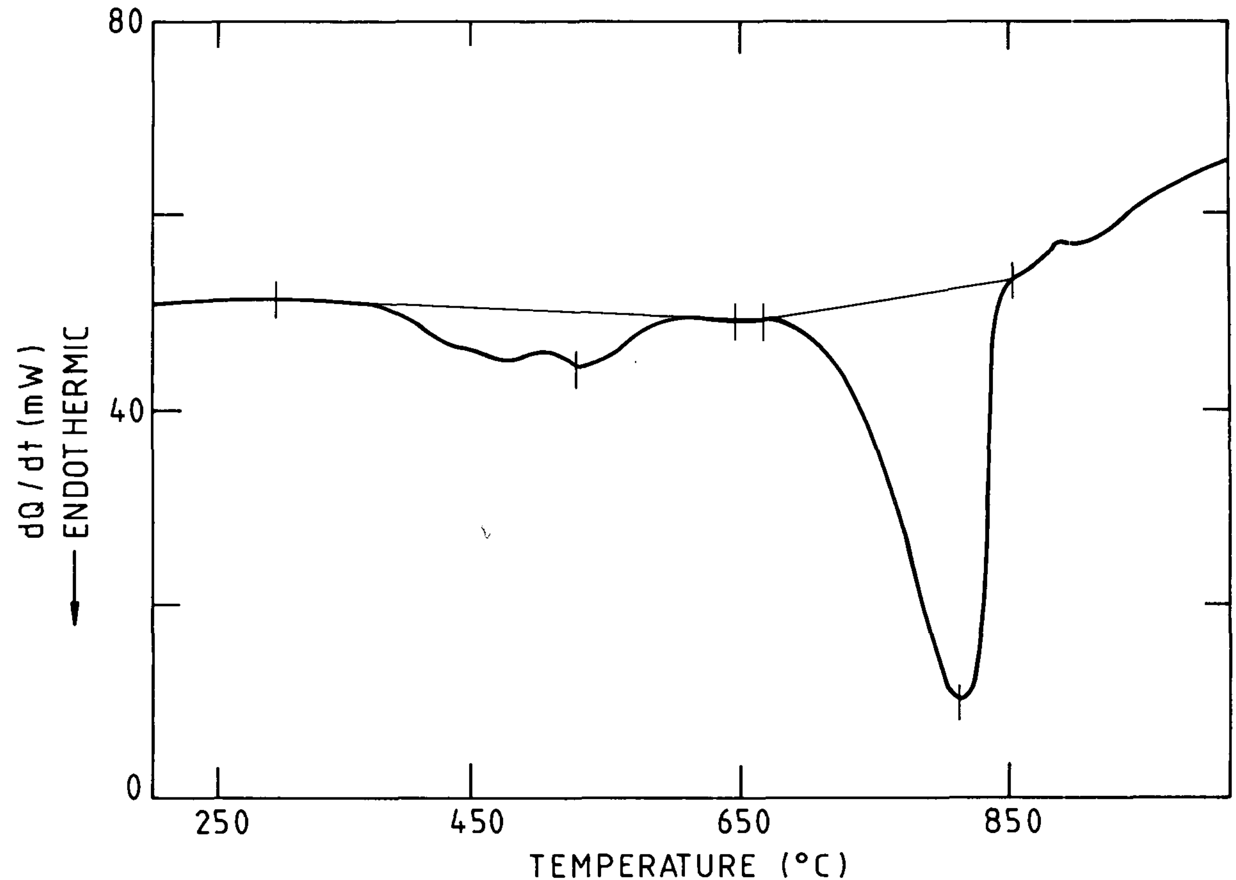

Figure 6. DSC curve for Julia Creek shale heated in nitrogen at 10°/min.

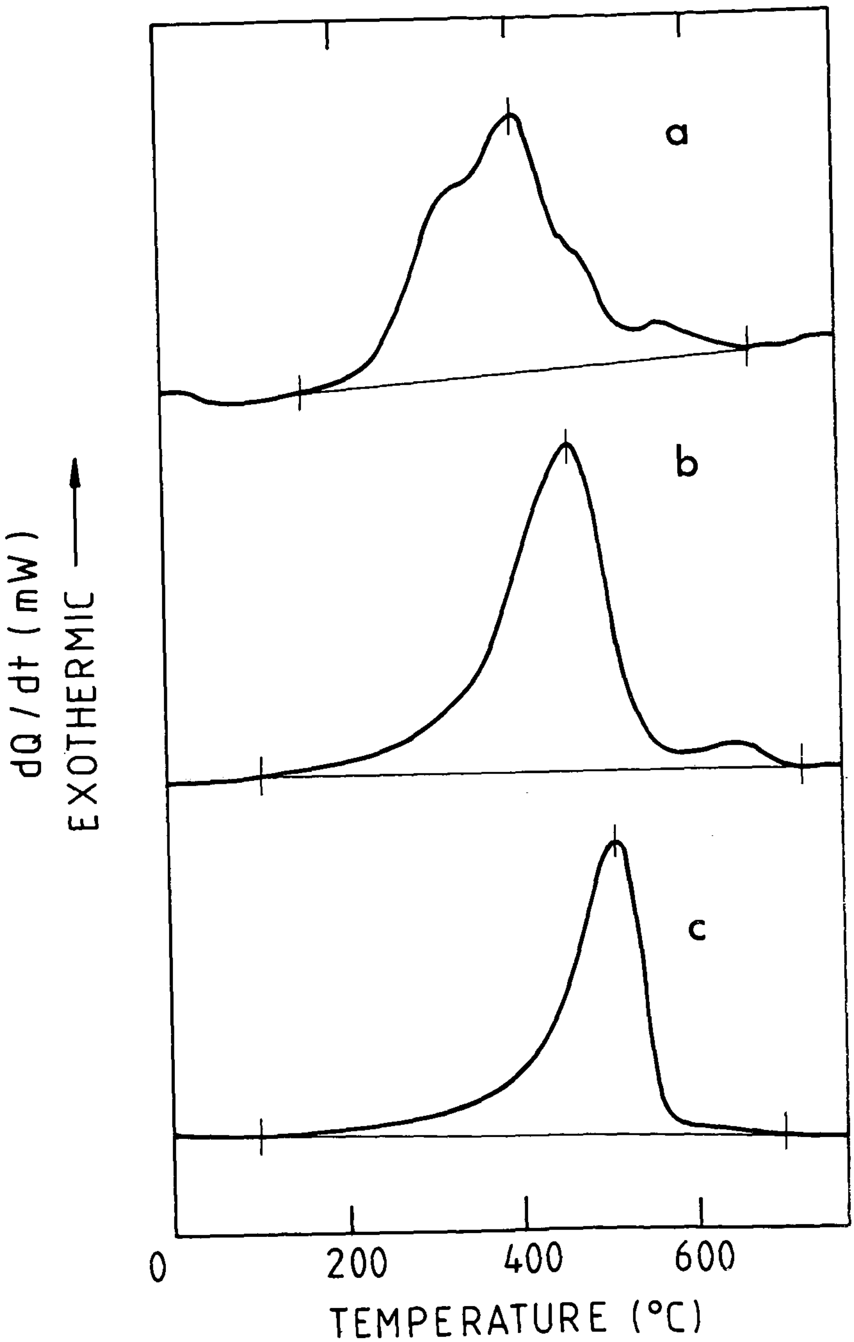

Figure 7. DSC combustion curves for Nagoorin shale and pyrolyzed residues heated in air at 10°/min.

a. Raw shale

b. Pyrolyzed residue (75% pyrolysis)

c. Pyrolyzed residue (100% pyrolysis)

not detectable at 910°C; so pyrolysis of Nagoorin carbonaceous kerogen beyond 75% is a process of carbonization to give a final char which retains about 50% of the initial kerogen mass.

TABLE IV

ENTHALPY OF COMBUSTION IN AIR OF NAGOORIN OIL SHALE AND ITS VARIOUS PYROLYZED RESIDUES OBTAINED BY HEATING THE SHALE AT 10°/MIN IN A DYNAMIC NITROGEN ATMOSPHERE

		Enthalpy of Combustion	
Final T	% Pyrolysis	MJ/kg Raw Shale	MJ/kg Pyrolyzed Residue
-	0	-11.0	-
300	8	-10.0	-10.9
580	75	- 8.6	-12.3
645	83	- 9.2	-13.5
780	97	- 8.3	-13.1
910	100	- 7.8	-12.6

Figure 7 shows DSC curves for combustion of the Nagoorin carbonaceous raw shale and some pyrolyzed residues. The combustion stages, shown clearly by DTG data, are not as well resolved in the DSC curve. Nevertheless, four exothermic stages can be distinguished for the raw shale, and identified by reference to TG-DTG profiles as discussed above. A major exothermic peak at 350°C is due principally to combustion of aliphatic components. The peak at 410°C corresponds to combustion of carbonaceous aromatic char, whilst two minor exotherms at higher temperatures arise from pyrite combustion. DSC curves for pyrolyzed residue show that with increasing pyrolysis, the first combustion peak diminishes and disappears, whereas the second peak shifts to higher temperatures. The fully pyrolyzed residue displays a single combustion peak at 509°C and the pyrite combustion exotherms are no longer evident; these may be eclipsed by peak shift but, more likely, decomposition of pyrite may have occurred during the final stages of pyrolysis.

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